Powerful Carnot cycle and attainability of the maximal efficiency

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We want to understand whether and to which extent the maximal (Carnot) efficiency for heat engines can be reached at a finite power. To this end we generalize the Carnot cycle so that it is not restricted to slow processes. We show that for realistic (i.e. not purposefully-designed) engine-bath interactions, the optimal engine performing the generalized Carnot cycle has a long cycle time and hence vanishing power. This aspect is shown to relate to the theory of computational complexity. A physical manifestation of the same effect is the Levinthal's paradox in the protein folding problem. The resolution of this paradox for realistic proteins allows to construct engines that can extract at a finite power 50 % of the maximally possible work reaching 90 % of the maximal efficiency. For purposefully-designed engine-bath interactions, the Carnot efficiency is achievable at a large power.

Reciprocating heat engines extract work operating cyclically between two thermal baths at temperatures T_1 and T_2 ($T_1 > T_2$) [1]. They have two basic characteristics: *(i)* efficiency, $\eta = W/Q_1$, is the work W extracted per cycle divided by the heat input Q_1 from the high-temperature bath. *(ii)* Power W/τ, where τ is the cycle duration. Both these quantities have to be large for a good engine: if η is small, lot of energy is wasted; if the power is small, no sizable work is delivered over a reasonable time [1].

The second law establishes the Carnot efficiency $\eta_C = 1 - \frac{T_2}{T_1}$ as an upper bound for η [1]. The Carnot cycle reaches the bounding value η_C in the (useless) limit, where the power goes to zero [1]. Conversely, realistic engines are not efficient, since they have to be powerful, e.g. the efficiency of Diesel engines amounts to 35–40 % of the maximal value. This *power-efficiency dilemma* motivated a search for the efficiency that would generally characterize the maximal power regime. One candidate for this is the Curzon-Ahlborn efficiency $\eta_{CA} = 1 - \sqrt{T_2/T_1}$ [2], which is however crucially tied to the linear regime $T_1 \approx T_2$ [3, 4]. Beyond this regime η_{CA} is a lower bound of η for a class of model engines [5]. Several recent models for the efficiency at the maximal power overcome η_{CA} with $\eta^* = \frac{\eta_C}{2 - \eta_C}$ [6].

As argued in [5, 7, 8], the maximal power regime allows for the Carnot efficiency, at least for certain models. But it is currently an open question whether the maximal efficiency is attained under realistic conditions (see e.g. [9] in connection with [7]), and how to characterize the very "realism" of those conditions. Even more generally: what is the origin of the power-efficiency dilemma? We answer them by analyzing a generalized Carnot cycle, which in contrast to the original Carnot cycle is not restricted to slow processes. We now summarize our answers.

(1) When the N-particle engine operates at the maximal work extracted per cycle, its efficiency reaches the Carnot bound η_C for $N \gg 1$, while the cycle time is given by the relaxation time of the engine. The maximal work and the Carnot efficiency are achieved due to the flat energy landscape of the engine. For realistic engine-bath interactions this energy landscape leads to very long [$\mathcal{O}(e^N)$] relaxation time nullifying the power. By realistic we mean interactions that are independent from the engine Hamiltonian. If we assume a proper tuning between engine-bath interaction and the engine Hamiltonian, the maximal efficiency is achievable at a large power $\mathcal{O}(\sqrt{N})$.

(2) The relaxation of the optimal engine under realistic interactions relates to an important problem of searching an unstructured database for a marked item, where each energy level refers to a database item. This task is computationally complex, i.e. even the most powerful quantum algorithms resolve it in $\mathcal{O}(e^{N/2})$ time-steps [11]. Hence the power-efficiency dilemma relates to computational complexity. The same effect can be reformulated as the Levinthal's paradox of the protein folding problem: if the majority of unfolded states of a protein are assumed to have the same (free) energy, the folding time is very long [12].

(3) A scenario of resolving the Levinthal's paradox proposed in protein science shows the way of constructing sub-optimal engines that operate at a reasonably large values of work, power and efficiency. These sub-optimal engines function as model proteins. Sacrificing some 50–60% of the maximal possible work leads to a reasonable relaxation times with the efficiency that achieves some 90 % of the maximal (Carnot) efficiency.

Carnot cycle and its generalization. Recall that the Carnot cycle consists of four slow, consecutive pieces [1]: thermally-isolated – isothermal – thermally-isolated – isothermal. Four times slow brings in the vanishing power stressed above. Since the overall process is a quasi-equilibrium one, the external fields that extract work from the engine act on it during all the four pieces. One deduces for the isothermal parts: $Q_1 = T_1 \Delta S$ and $Q_2 = T_2 \Delta S$, where Q_1 (Q_2) is the heat taken from (put into) the T_1-bath (T_2-bath), and $\Delta S > 0$ is the entropy change. Since the work extracted is $W = Q_1 - Q_2$, η

equals to its maximal value $\eta_C = 1 - \frac{T_2}{T_1}$ [1].

We keep the two isothermal and two thermally isolated pieces of the original Carnot cycle, but do not force them to be slow. In addition, the external fields will act only during the thermally isolated stages. Isothermal pieces amount to free relaxation; see Fig. 1. Due to this point, we shall be able to analyze the engine functioning from the energy conservation. We analyze the engine via quantum mechanics on a finite Hilbert space, because the inherently discrete character of quantum mechanics makes possible the optimization of the cycle (i.e. it reduces the problem to a combinatorial optimization). The final results are interpreted classically and can be also obtained by discretizing the Hamiltonian classical dynamics over phase-space cells.

0. The engine E with the Hamiltonian H_1 starts in an equilibrium state at temperature T_1 described by the density matrix

$$\rho(0) = \rho_1 = e^{-\beta_1 H_1}/(\operatorname{tr} e^{-\beta_1 H_1}), \quad \beta_1 = 1/T_1. \quad (1)$$

1. Between times 0 and τ, E undergoes a thermally isolated process with a time-dependent Hamiltonian $H_{12}(t)$ and the unitary evolution $\rho(\tau) = U_{12}\rho(0)U_{12}^\dagger$:

$$H_{12}(0) = H_1, \quad H_{12}(\tau) = H_2, \quad U_{12} = \mathcal{T}e^{-i\int_0^\tau ds H_{12}(s)}, (2)$$

where $\mathcal{T}$ means chronological ordering. The work taken out of E is determined by energy conservation [see [1] and section I of the Supplementary Material]

$$W_1 = \operatorname{tr}[H_1\rho_1 - H_2 U_{12}\rho_1 U_{12}^\dagger]. \quad (3)$$

2. Then E is attached to the T_2-bath and after relaxation time τ_r its density matrix becomes [see Fig. 1]

$$\rho(\tau + \tau_r) = \rho_2 = e^{-\beta_2 H_2}/(\operatorname{tr} e^{-\beta_2 H_2}). \quad (4)$$

The heat that came to E from the T_2-bath is

$$Q_2 = \operatorname{tr}[H_2\rho_2 - H_2 U_{12}\rho_1 U_{12}^\dagger]. \quad (5)$$

3. E undergoes another thermally isolated process

$$H_{21}(0) = H_2, \quad H_{21}(\tau) = H_1, \quad U_{21} = \mathcal{T}e^{-i\int_0^\tau ds H_{21}(s)}, (6)$$

completing the cycle with respect to the Hamiltonian. The work taken out of E reads

$$W_2 = \operatorname{tr}[H_2\rho_2 - H_1 U_{21}\rho_2 U_{21}^\dagger]. \quad (7)$$

4. Finally, E is attached to the T_1-bath ($T_1 > T_2$) and relaxes to ρ_1 thereby completing the cycle; see (1). The heat that came to E from the T_1-bath is

$$Q_1 = \operatorname{tr}[H_1\rho_1 - H_1 U_{21}\rho_2 U_{21}^\dagger]. \quad (8)$$

To stress the differences with the original Carnot cycle: (i) the cycle time $2(\tau + \tau_r)$ need not be much larger than the relaxation time τ_r. (ii) The cycle is out of equilibrium. (iii) The work source and the bath never act simultaneously; either one acts or another; see Fig. 1. Hence heat and work are deduced from the energy conservation.

The essential assumption of the cycle is that the system-bath coupling is weak; thus we did not count the work necessary for switching the coupling on and off.
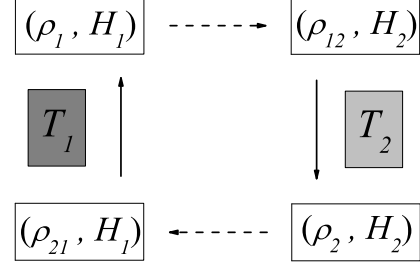

FIG. 1: Generalized Carnot cycle. Full (dashed) arrows refer to isothermal (thermally isolated) pieces. Thermal baths are denoted by T_1 and T_2. Four boxes carry notations for the state and Hamiltonian; see (1–8). The equilibrium states are $\rho_1 \propto e^{-H_1/T_1}$ and $\rho_2 \propto e^{-H_2/T_2}$. Also, $\rho_{12} = U_{12}\rho_1 U_{12}^\dagger$, $\rho_{21} = U_{21}\rho_2 U_{21}^\dagger$ are the states before isothermal pieces.

Maximization of work. We maximize the full extracted work $W = W_1 + W_2$ over H_1, H_2, U_{12}, U_{21} for fixed $T_1 > T_2$ and a fixed number $n+1$ of energy levels of E. The lowest energies of H_1 and H_2 can be set to zero. Then $W = W_1 + W_2$ reads from (3, 7)

$$W = \sum_{\alpha=1}^2 \sum_{k=2}^{n+1} p_k^{[\alpha]}\epsilon_k^{[\alpha]} \quad (9)$$

$$- \sum_{k,l=2}^{n+1} \left[\epsilon_k^{[1]}p_k^{[2]}C_{kl}^{[21]} + \epsilon_k^{[2]}p_k^{[1]}C_{kl}^{[12]}\right], \quad (10)$$

where the eigenvalues and eigenvectors of H_α are

$$H_\alpha = \sum_{k=2}^{n+1} \epsilon_k^{[\alpha]}|k^{[\alpha]}\rangle\langle k^{[\alpha]}|, \quad \alpha = 1, 2, \quad (11)$$

and where, given $\alpha, \gamma = 1, 2$ and $k, l = 1, ..., n+1$,

$$C_{kl}^{[\alpha\gamma]} = |\langle k^{[\alpha]}|U_{\alpha\gamma}|l^{[\gamma]}\rangle|^2, \quad (12)$$

$$p_k^{[\alpha]} = e^{-\beta_1\epsilon_k^{[\alpha]}}[1 + \sum_{k=2}^{n+1} e^{-\beta_1\epsilon_k^{[\alpha]}}]^{-1}. \quad (13)$$

$C_{kl}^{[\alpha\gamma]}$ are doubly stochastic matrices: $C_{kl}^{[\alpha\gamma]} \geq 0$, $\sum_{k=1}^{n+1} C_{kl}^{[\alpha\gamma]} = \sum_{l=1}^{n+1} C_{kl}^{[\alpha\gamma]} = 1$. Every doubly stochastic matrix C_{kl} can be represented as a convex sum of permutation matrices (Birkhoff's theorem) [14]: $C_{kl} = \sum_\delta \lambda_\delta \Pi_{kl}^{[\delta]}$, where $\lambda_\delta \geq 0$, $\sum_\delta \lambda_\delta = 1$, and where $\Pi^{[\delta]}$ permutes the components of any vector on which it acts.

Using Birkhoff's theorem we maximize W in (9, 10). The optimal $C_{kl}^{[12]}$ and $C_{kl}^{[21]}$ amount to permutation matrices, since they enter linearly into W. Hence they are unit matrices; see (10). In contrast to the original Carnot cycle, the optimal thermally isolated processes should

proceed very quickly, so that the Hamiltonian changes, but the density matrix does not; see (3, 7). The work

$$W = W_1 + W_2 = \sum_{k=2}^{n+1}(p_k^{[1]} - p_k^{[2]})(\epsilon_k^{[1]} - \epsilon_k^{[2]}), \quad (14)$$

is to be still maximized over $\{\epsilon_k^{[1]}\}_{k=2}^{n+1}$ and $\{\epsilon_k^{[2]}\}_{k=2}^{n+1}$; see (13). W is symmetric with respect to permutations within $\{\epsilon_k^{[1]}\}_{k=2}^{n+1}$ and within $\{\epsilon_k^{[2]}\}_{k=2}^{n+1}$. We checked numerically that this symmetry is not broken and hence the maximum of W is reached for

$$\epsilon^{[\alpha]} \equiv \epsilon_2^{[\alpha]} = ... = \epsilon_{n+1}^{[\alpha]}, \quad \alpha = 1, 2, \quad (15)$$

i.e. all excited levels have the same energy. With new variables $e^{-\beta_\alpha \epsilon^{[\alpha]}} \equiv u_\alpha$ we write the maximal work as

$$W_{\max}[u_1, u_2] = \frac{(T_1 \ln \frac{1}{u_1} - T_2 \ln \frac{1}{u_2})(u_1 - u_2)n}{[1 + nu_1][1 + nu_2]}, \quad (16)$$

where u_1 and u_2 are found from

$$\partial_{u_1} W_{\max}[u_1, u_2] = \partial_{u_2} W_{\max}[u_1, u_2] = 0. \quad (17)$$

u_1 and u_2 depend on T_2/T_1 and on n. Noting (8) and the result before (14) we obtain $Q_1 = \text{tr}(H_1(\rho_1 - \rho_2))$ for the heat obtained from the high-temperature bath. Using (15) we get from $\eta = W/Q_1$ and from (16):

$$\eta = 1 - [T_2 \ln u_2]/[T_1 \ln u_1]. \quad (18)$$

Note from (16) that $W_{\max}[u_1, u_2] > 0$ and $T_2 < T_1$ imply $1 > \epsilon^{[2]}/\epsilon^{[1]} > T_2/T_1$. Hence (18) implies $\eta \le \eta_C = 1 - T_2/T_1$, as expected.

Thus the thermally isolated pieces of the cycle consist, respectively, of sudden changes $\epsilon^{[1]} \to \epsilon^{[2]}$ and $\epsilon^{[2]} \to \epsilon^{[1]}$. This is an advantage, since sudden changes are automatically thermally isolated (no time to interact with the baths). In contrast, a slow thermally isolated change is difficult to realize, which is one of the reasons for the original Carnot cycle being practically useless [1].

Both $W_{\max}[u_1, u_2]$ and η increase with n. For $\ln[n] \gg 1$ we get asymptotically from (17):

$$u_1 = \frac{(1-\theta)\ln[n]}{n}, \quad u_2 = \frac{\theta}{n\ln[n](1-\theta)}, \quad (19)$$

where $\theta \equiv T_2/T_1$. This produces

$$W_{\max}[u_1, u_2] = (T_2 - T_1)\ln[n] - \mathcal{O}(1/\ln[n]), \quad (20)$$
$$\eta = \eta_C - \mathcal{O}(1/\ln[n]), \quad \eta_C \equiv 1 - T_2/T_1. \quad (21)$$

The maximal work $W_{\max}[u_1, u_2]$ scales as $\ln[n]$, since this is the "effective number of particles" for the engine. In the macroscopic limit $\ln[n] \gg 1$, the efficiency converges to its maximal value $\eta_C = 1 - T_2/T_1$; see (21). Recall from (15) that nu_α is the overall probability of the excited levels. Hence for $\ln[n] \gg 1$ the ground state (excited levels) dominates in ρ_2 (ρ_1); see (19).

The cycle time amounts to two times the relaxation time τ_r of the system with spectrum (15) and energy gap $\epsilon \sim \ln[n]$; see (15, 19). (Recall that the thermally isolated stages of the cycle are very quick.) The magnitude of τ_r essentially depends on the scenario of relaxation.

First (specific) scenario. We can assume that the Hamiltonian (11, 15) of the heat engine is known. Then there exist system-bath interaction scenarios that lead to $\tau_r = \mathcal{O}(\sqrt{\ln[n]})$; section IV of the Supplementary Material. Hence for this type of relaxation the Carnot efficiency is achievable at a large power $\mathcal{O}(\sqrt{\ln[n]}) \gg 1$; see (20). However, in these scenarios the system-bath interaction Hamiltonian (that governs the relaxation) is special: it depends on the engine Hamiltonian (11, 15).

Second (realistic) scenario. Assuming that the system-bath interaction does not depend on the Hamiltonian (11, 15), we can estimate τ_r within the weak-coupling, Markov master equation approach that leads to $\tau_r = \mathcal{O}(n)$; section II of the Supplementary Material. For a qualitative understanding of this situation, consider the relaxation as a random walk in the energy space, e.g. in the second step of the cycle, system starts with its vacuum being, according to (19), almost unpopulated and it has to relax to a state in which the probability of the ground state is almost 1. So, if every transition from one excited energy level to another takes a finite time, one will need to perform in average $n/2$ transitions before visiting the ground state. Now note from (21) that the convergence of η to η_C is controlled by $\mathcal{O}(1/\ln[n])$: a small step towards η_C will lead to a large increase in τ_r nullifying the power $\mathcal{O}(\ln[n]/n)$ for $n \gg 1$; see (20). Hence for this type of relaxation the Carnot efficiency is not achievable at a finite power.

The second relaxation scenario of the system with Hamiltonian (11, 15) is similar to the known combinatorial optimization problem: finding a marked item in an unstructured database [11] of $n + 1$ items. This problem is mapped to physics by associating each item to an eigenvector of a Hamiltonian. The marked item relates to the lowest energy level 0, while all other (excited) eigenvalues of the Hamiltonian ϵ are equal. The resulting system has unknown eigenvectors of the Hamiltonian, but known eigenenergies. Now the searching process can be organized as a relaxation of the system from an excited state to a low-temperature equilibrium state. This state is dominated by the ground level due to a large ϵ. Once the relaxation is over the unknown item (eigenvector) can be revealed by measuring the energy [15].

Within classical physics the minimal search time of this problem scales as $\mathcal{O}(n)$ for $n \gg 1$ [11]. It is thus not much better than going over all possible candidates for the solution, a typical situation of a computationally complex problem. For quantum algorithms (Grover's search) the search time scales as $\mathcal{O}(\sqrt{n})$ [11]. This is smaller than the classical estimate $\mathcal{O}(n)$, but it still not suitable for our purposes, since it nullifies the power for $\ln[n] \gg 1$.

Sub-optimal engine. Within the second (realistic) relaxation scenario, we shall modify the optimal engine so that the power is finite, but both the work and efficiency are still large. We are guided by the analogy between the relaxation of the Hamiltonian (11, 15) under the second scenario and the Levinthal's paradox from protein physics [12]. In fact, (11, 15) is the simplest model employed for illustrating the paradox [13]. Here the ground state refers to the unique folded (native) state. To ensure its stability, it must be separated by a large gap from excited (free) energy levels. The essence of the paradox is that assuming the existence of many *equivalent* excited (unfolded) states, the relaxation time to the native state will be unrealistically long. Recall that the states ρ_1 and ρ_2 of the optimal engine refer respectively to unfolded and folded states of the protein model; see after (21).

The resolution of the paradox is to be sought via resolving the degeneracy of excited levels: if there are energy differences, some (unfavorable) transitions will not be made shortening the relaxation time [13]. In resolving the energy degeneracy we follow the basic model proposed for resolving the paradox [12].

The model has $N \gg 1$ degrees of freedom $\{\sigma_i\}_{i=1}^n$; each one can be in $\zeta + 1$ states: $\sigma_i = 0, ..., \zeta$. Whenever $\sigma_i = 0$ for all i's, the model protein is in folded (ground) state with energy zero [12, 13]. The ground state has zero energy. Excited states with $s \geq 1$ have energy $\epsilon + \delta s$, where $\epsilon > 0$ and s is the number of (misfolded) degrees of freedom with $\sigma_i \neq 0$. $\delta > 0$ is the parameter that (partially) resolves the degeneracy of excited states; we revert to the previous, work-optimal model for $\delta \to 0$. Thus for the Hamiltonians H_1 and H_2 we have

$$H_\alpha(s) = [0, \{\epsilon^{[\alpha]} + s\delta^{[\alpha]}\}_{s=1}^N], \quad \alpha = 1, 2, \qquad (22)$$

where each energy $\epsilon^{[\alpha]} + s\delta^{[\alpha]}$ is degenerate $\frac{\zeta^s N!}{s!(N-s)!}$ times.

Given (22), the functioning of the cycle consists of two isothermal and two thermally isolated pieces with sudden changes $(\delta^{[1]}, \epsilon^{[1]}) \to (\delta^{[2]}, \epsilon^{[2]}) \to (\delta^{[1]}, \epsilon^{[1]})$. Thus (1–14) remain true. Recall that they determine the generalized Carnot cycle that is optimal with respect to the thermally isolated pieces. Below we shall also assume

$$\beta_1 \delta^{[1]} = \beta_2 \delta^{[2]}, \qquad (23)$$

because this makes the sub-optimal engine structurally very similar to the optimal one. Now the work $W = W_1 + W_2$ is calculated from (3, 7, 8, 22, 23):

$$W[v_1, v_2; K] = \frac{m(\Delta\epsilon + \frac{KN\Delta\delta}{1+K})(v_1 - v_2)}{(1 + mv_1)(1 + mv_2)}, \quad (24)$$

$$\Delta\epsilon = \epsilon^{[1]} - \epsilon^{[2]} = T_1 \ln[1/v_1] - T_2 \ln[1/v_2], \quad (25)$$

$$\Delta\delta = \delta^{[1]} - \delta^{[2]} = (T_1 - T_2) \ln[\zeta/K]. \qquad (26)$$

where $K = \zeta e^{-\beta_1 \delta^{[1]}}$, $m = (1 + K)^N$, and where $v_\alpha \equiv e^{-\beta_\alpha \epsilon^{[\alpha]}}$ ($\alpha = 1, 2$) are determined from maximizing (24).

TABLE I: Parameters of the sub-optimal engine—work W, efficiency η and the cycle time $2\tau_r$—versus those of the optimal one; see (24–28). $W_{\max}$ is the maximal work extracted for $K = \zeta e^{-\beta_1 \delta^{[1]}}$ at a vanishing power; see (16, 17). $N = 140$, $\zeta = 4$, $T_1 = 1$, $T_2 = 1/2$. Carnot efficiency $\eta_C = 1/2$. The Curzon-Ahlborn efficiency for this case is $0.5858\eta_C$. $p_1^{[\alpha]} = [1 + (1 + K)^N e^{-\beta_\alpha \epsilon^{[\alpha]}}]^{-1}$ (for $\alpha = 1, 2$) are the ground-state probabilities of $\rho_\alpha \propto e^{-\beta_\alpha H_\alpha}$; see (22).

K	τ_r	$W/W_{\max}$	W	η/η_C	$p_1^{[1]}$	$p_1^{[2]}$
0.1	4.45×10^{-5} s	0.2267	23.52	0.8751	0.0392	0.9808
0.2	4.35 s	0.3884	40.3	0.9110	0.0237	0.9883
0.24	357 s	0.4393	45.58	0.9181	0.0210	0.9896

Note the analogy between (16) and (24), with m being an analogue of n; they get equal for $\delta \to 0$. Note that in (24) we neglected factor $\mathcal{O}(\frac{1}{m})$ assuming that $m \gg 1$.

Likewise, we get for the efficiency:

$$\eta = 1 - \frac{T_2}{T_1} \times \frac{\ln\frac{1}{v_2} + \frac{NK\ln(v/K)}{1+K}}{\ln\frac{1}{v_1} + \frac{NK\ln(v/K)}{1+K}}. \qquad (27)$$

For this model [12] assumes a local Markov relaxation dynamics, where each degree of freedom makes a transition $\sigma_i \to \sigma_i \pm 1$ in 10^{-9} seconds; this value is chosen conventionally to fit experimental magnitudes for the elementary dynamic step [12]. The model has a single relaxation time [12] that is easily reproduced in the general master-equation framework [section III of the Supplementary Material]:

$$\tau_r = 10^{-9}(1 + K)^N/(NK) \text{ seconds}, \qquad (28)$$

where the factor N is due to the N-times degenerate first excited level.

For $\delta^{[\alpha]} \to 0$ ($\alpha = 1, 2$), where the excited energy levels become degenerate, $\tau_r \propto (1 + \zeta)^N$ scales linearly over the number of energy levels, as expected. When $\delta^{[\alpha]}$ are not zero, τ_r can be of order of 1 second for $N \sim 100$, because $1 + K$ is close to 1. However, for the macroscopic situation ($N \sim 10^{23}$) τ_r is still huge. In this sense, the model is incomplete, but still useful for analyzing the mesoscopic situation $N \sim 100$ that is relevant for the protein folding problem [13].

Table I illustrates the characteristics of the sub-optimal engine and compares them with those of the optimal one. It is seen that a reasonable cycle times can coexist with a finite fraction ($\sim 40\%$) of the maximal work and with large efficiencies ($\sim 90\%$) of the maximal value that is definitely larger than e.g. the Curzon-Ahlborn value). Hence, albeit within the second (realistic) scenario it is impossible to approach the maximal efficiency as close as desired, reasonably large efficiencies at a finite (or

even large) power are still possible. These results resemble the power-efficiency trade-off (see [10]), but they are more complicated, since they involve work, efficiency and power.

Summary. The generalized Carnot cycle allows to understand why the Carnot efficiency at a finite power is not realized in practice: it relates to the computational complexity that enforces very large cycle times. As we argued, this does not mean that finite-power and Carnot efficient engines are impossible to built in principle; it is that they are not met under realistic conditions. Even then, it is useful to study the optimal-work-efficiency engines: though they have an unrealistically long cycle time, their straightforward improvements do produce models working at reasonably large efficiency (and finite power). These sub-optimal models coincide with those of good folded proteins. We shall return elsewhere to biophysical implications of this fact.

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Supplementary material

This material consists of four sections. Section I relates together two definitions of work. Section II estimates the relaxation time of the optimal engine within the master-equation framework (first scenario of relaxation). Section III does the same for the sub-optimal engine. Section IV discusses an example of the first relaxation scenario and shows that the relaxation time of the optimal engine within this scenario is much shorter than the best estimate within the second scenario.

I. CLARIFICATION OF THE CONCEPT OF WORK AS USED IN OUR SITUATION.

Let a system interact with a source of work only (thermally isolated process). This means that the system Hamiltonian $H[\alpha(t)]$ is a function of a (classical) parameter $\alpha(t)$. The work done on the system per unit of time equals to "force" times "displacement" and averaged over state of the system, as represented by a time-dependent density matrix $\rho(t)$:

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \frac{\mathrm{d}\alpha(t)}{\mathrm{d}t}\mathrm{tr}\left(\frac{\partial H}{\partial \alpha}\rho(t)\right). \tag{29}$$

The same formula applies in the classical situation, where tr means integration over the phase-space (the space of coordinates and momenta), while ρ becomes the phase-space probability density. Now one can use the equations of motion for the density matrix, $i\hbar\frac{\mathrm{d}\rho}{\mathrm{d}t} = H[\alpha(t)]\rho(t) - \rho(t)H[\alpha(t)]$ (in the classical situation this becomes the Liouville equation), to show from (29) that the total work equals to the change of average energy

$$W(\tau) = \int_0^\tau \mathrm{d}t\,\frac{\mathrm{d}W}{\mathrm{d}t} = \mathrm{tr}\left(H[\alpha(\tau)]\rho(\tau) - H[\alpha(0)]\rho(0)\right). \tag{30}$$

II. RELAXATION TIME OF THE OPTIMAL ENGINE VIA MASTER EQUATION

Consider a system with $n \gg 1$ degenerate (excited) levels with energy $\varepsilon > 0$, and a single ground state with energy 0. The relaxation time of this system can be estimated via the master equation. Let $\{p_i\}_{i=0}^n$ be the probability of energy levels. The master equation reads

$$\dot{p}_0 = \sum_{i=1}^n w_{0i}p_i - p_0\sum_{i=1}^n w_{i0}, \tag{31}$$

where w_{0i} is rate of the transition $i \to 0$. Since all energy levels besides the lowest one have the same energy ε, both $w_{0i} = w_{01}$ and $w_{i0} = w_{10}$ do not depend on i. The rates relate to each other via the detailed balance conditions (which reflects the fact that the bath is in equilibrium at temperature $1/\beta$):

$$w_{01}e^{-\beta\varepsilon} = w_{10}. \tag{32}$$

In addition, since all the excited energy levels are equivalent, w_{01} and w_{10} have an overall dependence $\mathcal{O}(\frac{1}{n})$:

$$w_{01} = \hat{w}_{01}/n, \quad w_{10} = \hat{w}_{10}/n, \tag{33}$$

where $\hat{w}_{10}$ and $\hat{w}_{01}$ do not depend on n. The origin of (33) is that (apart of the energy difference between the ground state and an excited state) the transition takes place with a equal probability to (from) any excited energy level. We end up from (31–33) with

$$\dot{p}_0 = -w_{01}p_0[ne^{-\beta\varepsilon} + 1] + w_{01}, \qquad (34)$$

meaning that the relaxation time τ_r for $p_0(t)$ to converge to its equilibrium value

$$p_0^{[eq]} = 1/(1 + ne^{-\beta\varepsilon}) \qquad (35)$$

reads

$$1/\tau_r = \hat{w}_{01}[ne^{-\beta\varepsilon} + 1]/n. \qquad (36)$$

We are interested in the situation, where the equilibrium probability (35) of the ground-state is sizable. More precisely in our situation $e^{-\beta\varepsilon} = \mathcal{O}(\ln[n]/n)$ or $e^{-\beta\varepsilon} = \mathcal{O}(\frac{1}{n\ln[n]})$. At any rate, the relaxation time τ_r in (36) is roughly $\mathcal{O}(n)$.

III. RELAXATION TIME OF SUB-OPTIMAL ENGINES VIA ADIABATIC APPROXIMATION OF THE MASTER EQUATION

We return to (31), but we do not assume anymore that the excited levels $\varepsilon_1, ..., \varepsilon_n$ have the same energy. But we still assume that the gap $\varepsilon_1 > 0$ between the zero-energy ground state and the first excited state is the largest energy parameter in the system, because we want to ensure that the equilibrium ground-state probability is close to 1. Thus we may apply to (31) the adiabatic approximation assuming that on those times where p_0 changes, the excited-state probabilities p_i already equilibrated:

$$p_i(t) = (1 - p_0(t))e^{-\beta\varepsilon_i} \Big/ \sum\nolimits_{i=1}^{n} e^{-\beta\varepsilon_i} . \qquad (37)$$

Hence the relaxation time τ_r of p_0 deduced from (31, 37) reads

$$\frac{1}{\tau_r} = \frac{\sum_{i=1}^{n} w_{0i}e^{-\beta\varepsilon_i}}{\sum_{i=1}^{n} e^{-\beta\varepsilon_i}} + \sum_{i=1}^{n} e^{-\beta\varepsilon_i}w_{0i}, \qquad (38)$$

where the employed the detailed balance condition.

Eq. (38) reproduces the relaxation time (28) of the Zwanzig model [12], if we employ the energy spectrum (22) and note that the transition probabilities from the first excited (ζN-degenerate) energy level are constants, $w_{0k} = 10^9$ for $k = 1, ..., \zeta N$, while no transitions (to the ground state) is possible from other excited states: $w_{0l} = 0$ for $l = \zeta N + 1, ..., n$. Here 10^9 is the characteristic microscopic scale [12]. Putting these into (38) we get that the first term in the right-hand-side of (38) reproduces (28). The second term is neglegible, if $e^{-\beta\varepsilon_1}$ is sufficiently small.

Note that according to (28), the relaxation time of the Zwanzig model is still unacceptably large, if $N \gg 1$. It is not difficult to get rid of this restriction, though it is not useful from the viewpoint of the heat engine functioning, where a large parameter is needed.

IV. AN EXAMPLE OF THE FIRST RELAXATION SCENARIO

System-bath interaction

Consider a system E with n excited energy levels and one lowest energy (ground state) whose energy we set to zero. All n excited levels have the same energy ϵ.

The initial density matrix of E is Gibbsian at temperature $T_0 = 1/\beta_0$:

$$\rho \propto e^{-\beta_0 H} = r\mathcal{P}_0 + \frac{1-r}{n}\mathcal{P}_\epsilon, \qquad (39)$$

$$r = \frac{1}{1 + ne^{-\beta_0\epsilon}}, \qquad (40)$$

where $\mathcal{P}_0 = |0\rangle\langle0|$ is the projector on the ground state, and $\mathcal{P}_\epsilon$ is the projectors on the n-dimensional eigen-space of ρ with eigenvalue ϵ.

Now E interacts with an external thermal bath at temperature $T = 1/\beta$, so that the density matrix of E converges in time to $\rho_{eq} \propto e^{-\beta H}$. We shall design a concrete model for this interaction and estimate the relaxation time.

We assume that the bath consists of a large number of independent particles prepared in identical (thermal states). E interacts with one particle, then with the second one *etc.* Since the particles are independent, it will suffice to consider the interaction of E with the first particle B only.

We assume that the bath particle B has (among other energies) energy levels E and $E + \varepsilon$. The degeneracies of these levels are n_E and $n_{E+\varepsilon}$, respectively. The initial (before interacting with E) equilibrium density matrix of B reads

$$\sigma = e^{-\beta H_B}/Z = \widetilde{\sigma} + r_E\,\Pi_E + r_{\epsilon+E}\,\Pi_{\epsilon+E}, \qquad (41)$$

$$r_E = e^{-\beta E}/Z, \quad Z = \sum\nolimits_E n_E e^{-\beta E}, \qquad (42)$$

where r_E and $r_{E+\varepsilon}$ are the Boltzmann weights for the energy levels E and $E + \varepsilon$, respectively, the summation in (42) is taken over all energy levels of B. Π_E and $\Pi_{\varepsilon+E}$ are the projectors on the corresponding sub-spaces,

$$\text{tr}\,\Pi_E = n_E, \qquad \text{tr}\,\Pi_{\varepsilon+E} = n_{E+\varepsilon}, \qquad (43)$$

and where $\widetilde{\sigma}$ in (41) is the remainder of σ.

It is assumed that the unitary operator $\mathcal{V}$ responsible for the interaction operates within the sub-space with the projector $\mathcal{P}_\varepsilon \otimes \Pi_E + \mathcal{P}_0 \otimes \Pi_{E+\varepsilon}$ (this sub-space has energy $E + \varepsilon$), i.e.,

$$[\mathcal{V}, \mathcal{P}_\varepsilon \otimes \Pi_E + \mathcal{P}_0 \otimes \Pi_{E+\varepsilon}] = 0. \qquad (44)$$

On the remainder of the overall Hilbert space (of E+B) $\mathcal{V}$ acts as unit operator. Thus, $\mathcal{V}$ commutes with the Hamiltonian of E+B. Hence no additional energy (work) is needed for switching the E-B interaction on and off. In that respect $\mathcal{V}$ resembles the weak-coupling, though by itself it need not be weak, i.e. it need not be smaller than the Hamiltonian of E+B.

Then the post-interaction density matrix ρ' of E reads

$$\begin{aligned} \rho' &= \text{tr}_B \mathcal{V}\rho \otimes \sigma\mathcal{V}^\dagger \\ &= \rho - \left(r\,r_{E+\varepsilon} - r_E\frac{1-r}{n}\right) \times \\ &\quad [n_{E+\varepsilon}\mathcal{P}_0 - \text{tr}_B\mathcal{V}\mathcal{P}_0 \otimes \Pi_{E+\varepsilon}\mathcal{V}^\dagger]. \end{aligned} \qquad (45)$$

It will suffice to keep track of the lowest energy-level occupation $\langle 0|\rho'|0\rangle \equiv r'$ only:

$$r' - r = -A\left[r - r_{eq}\right], \quad r_{eq} \equiv \frac{1}{1 + ne^{-\beta\varepsilon}}, \quad (46)$$

$$A \equiv \frac{r_E}{r_{eq}n}\left[n_{E+\varepsilon} - \langle 0|\left(\mathrm{tr_B}\mathcal{V}\mathcal{P}_0 \otimes \Pi_{E+\varepsilon}\mathcal{V}^\dagger\right)|0\rangle\right], \quad (47)$$

where r_{eq} is the equilibrium value of r. Using (42) one can show that $A \leq A_{max} \leq 1$: after the interaction E gets closer to its equilibrium state; see (46).

Now (45) serves as the initial state of E for a similar interaction with the second bath particle that initially has the same state σ as in (41). We get for all subsequent interactions [we revert from (48) to (46) for $m = 1$]:

$$r^{[m]} - r_{eq} = (1 - A)^m\left[r - r_{eq}\right], \quad (48)$$

It is seen that (48) predicts exponential (with respect to the number of collisions) relaxation towards the equilibrium value r_{eq} of r. The approach to equilibrium is governed by the factor $(1 - A)^m$ meaning that when $|A| \ll 1$ the effective number of interactions after which the equilibrium is established (which is proportional to the relaxation time) equals to $-1/[\ln(1 - A)]$.

Minimization of the relaxation time

Since we are interested in possibly shorter relaxation time, we need to maximize A over the unitary $\mathcal{V}$ [under condition (44)]. To do that, we first write $P_0 \otimes \Pi_{E+\varepsilon}$ in a conveniently chosen matrix form in the energy eigenbasis

$$P_0 \otimes \Pi_{E+\varepsilon} = \quad (49)$$
$$\mathrm{diag}(\underbrace{..., 1, ..., 1, ...}_{n_{E+\epsilon} \text{ elements}} | \underbrace{..., 0, ..., 0, ...| \cdots |..., 0, ..., 0, ...}_{n \text{ sections}}), \quad (50)$$

where sections correspond to eigenvectors of H, and elements in sections run over the ones of H_B. Values are shown only for the subspace given by $P_0 \otimes \Pi_{E+\varepsilon} + P_\varepsilon \otimes \Pi_E$. The first section (denoted as $|...|$) there are $n_{E+\varepsilon}$ unities. Then come n identical sections, each one contains n_E zeroes.

To maximize A we need to minimize $\langle 0|\left(\mathrm{tr_B}\mathcal{V}\mathcal{P}_0 \otimes \Pi_{E+\varepsilon}\mathcal{V}^\dagger\right)|0\rangle$ over all possible $\mathcal{V}$s living in $P_0 \otimes \Pi_{E+\varepsilon} + P_\varepsilon \otimes \Pi_E$. One can show that the optimal unitary amounts to a permutation of the eigenvalues (50) (this fact can be shown similarly to the derivation presented in (9-13) of the main text). Now we note that the trace over tr_B amounts to summing up elements in each section. So the element $\langle 0|\left(\mathrm{tr_B}\mathcal{V}\mathcal{P}_0 \otimes \Pi_{E+\varepsilon}\mathcal{V}^\dagger\right)|0\rangle$ will be the sum of the elements of the first section in the permuted diagonal in (49). The optimal permutation will thus be the one which takes out of the first section as much unities as possible. Therefore, if $n_{E+\varepsilon}$ (the number of unities) is $<$ than $n_E n$—the number of zeroes—then it is possible to move all unities, making $\min_\mathcal{V}\left\{\langle 0|\left(\mathrm{tr_B}\mathcal{V}\mathcal{P}_0 \otimes \Pi_{E+\varepsilon}\mathcal{V}^\dagger\right)|0\rangle\right\} = 0$. Otherwise, the latter quantity will be $n_{E+\varepsilon} - n_E n$, leading us to the following formula:

$$A_{max} = \frac{r_E \min\left[n_{E+\varepsilon}, n_E n\right]}{r_{eq}n}. \quad (51)$$

Relaxation time for realistic bath

Let us work out (51) for a realistic example of the bath. We assume that the bath particle amounts to $L \gg 1$ independent two-level systems. Each such system has energies 0 and ζ. Thus the bath particle has energies $0, \zeta, 2\zeta, ..., L\zeta$. Each bath energy level E is degenerate

$$n_E = \frac{L!}{(E/\zeta)!(L - E/\zeta)!} \quad (52)$$

times. Provided that

$$n_{E+\varepsilon} > n_E n, \quad (53)$$

we obtain

$$A_{max} = (1 + ne^{-\beta\varepsilon})\frac{n_E e^{-\beta E}}{Z}. \quad (54)$$

Since we want a larger A_{max}, we take

$$E = L/(e^{\beta\zeta} + 1). \quad (55)$$

Hence using the Stirling's formula $L! \simeq \sqrt{2\pi L}\, L^L e^{-L}$ and noting that $Z = (1 + e^{-\beta\zeta})^L$ we get from (54)

$$A_{max} \simeq (1 + ne^{-\beta\epsilon})\sqrt{\frac{1 + e^{-\beta\zeta}}{L}}. \quad (56)$$

We work out (53) via the Stirling's formula and obtain from (53, 55)

$$\frac{\ln[n]}{L} + h_2[\frac{1}{e^{\beta\zeta} + 1}] < h_2[\frac{1}{e^{\beta\zeta} + 1} + \frac{\epsilon}{L\zeta}], \quad (57)$$

where $h_2[x] = -x\ln x - (1 - x)\ln(1 - x)$.

Let us specify ϵ as [μ is a parameter]

$$\epsilon = \mu T \ln[n], \quad \mu > 1. \quad (58)$$

Putting this into (57) we get

$$\frac{\ln[n]}{L} + h_2[\frac{1}{e^{\beta\zeta} + 1}] < h_2[\frac{1}{e^{\beta\zeta} + 1} + \frac{\mu}{\beta\zeta}\frac{\ln[n]}{L}]. \quad (59)$$

Provided that $\mu > 1$, (59) can be satisfied for sufficiently small (but finite) $\frac{\ln[n]}{L}$ and sufficiently large $\zeta > 0$. Note that (59) never holds for $\mu \leq 1$.

Returning to (56) we see from (58) that for $\ln[n] = \mathcal{O}(L) \gg 1$

$$A_{max} = \mathcal{O}(\frac{1}{\sqrt{\ln[n]}}), \quad (60)$$

which means that the relaxation time scales as $\mathcal{O}(\sqrt{\ln[n]})$.

Consider now the opposite [to (53)] case

$$n_{E+\varepsilon} < n_E n, \quad (61)$$

where

$$A_{max} = (1 + \frac{1}{ne^{-\beta\epsilon}})\frac{n_{E+\epsilon}e^{-\beta(E+\epsilon)}}{Z}. \quad (62)$$

Choosing

$$E + \epsilon = L/(e^{\beta\zeta} + 1), \quad (63)$$

we get [cf. (56)]

$$A_{\max} \simeq (1 + \frac{1}{ne^{-\beta\epsilon}}) \sqrt{\frac{1 + e^{-\beta\zeta}}{L}}. \qquad (64)$$

If we specify [cf. (58)]

$$\epsilon = \nu T \ln[n], \quad \nu < 1, \qquad (65)$$

then (61) reads [cf. (59)]

$$h_2[\frac{1}{e^{\beta\zeta} + 1}] < \frac{\ln[n]}{L} + h_2[\frac{1}{e^{\beta\zeta} + 1} - \frac{\nu}{\beta\zeta} \frac{\ln[n]}{L}]. \qquad (66)$$

This relation holds for $\nu < 1$, sufficiently small (but finite) $\frac{\ln[n]}{L}$ and sufficiently large $\zeta > 0$.
Hence from (66, 62) we return to the same conclusion (60).

Relations with the main text

In the main text—see in particular (16, 19)— we studied the relaxation of the optimal engine E that has the energy spectrum described at beginning of section IV. More specifically, in the main text we needed two different relaxation scenario: E with energy gap $\epsilon^{[1]} \simeq T_1 \ln[n]$ relaxes on a thermal bath at temperature T_2 (where $T_1 > T_2$), and conversely E with energy gap $\epsilon^{[2]} \simeq T_2 \ln[n]$ relaxes on a thermal bath at temperature T_1; see (19) of the main text in this context.
Now the first case corresponds to (58, 59, 60), while the second case to (65, 66, 60). In both cases we get that for a realistic thermal thermal bath (but with tuned system-bath interactions) the relaxation time amounts to $\mathcal{O}(\sqrt{\ln[n]})$; see (60).